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Decomposition of Feldspar by Lime

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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ENTITLED Decomposition of Feldspar by Means of Lime under Pressure, and Extraction of Potash.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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DECOMPOSITION OF FELDSPAR BY MEANS OF LIME UNDER PRESSURE, AND EXTRACTION OF POTASH.

INTRODUCTION.

During the last six years, a series of investigations has been carried on at the University of Illinois on the reaction of silica with lime at high steam pressure, or more generally on the formation of artificial silicates at steam temperatures. The work was started in 1905 by Mr. C. F. Hagedorn[1] in the division of applied chemistry under the direction of Professor S. W. Parr. Hagedorn attempted to make silica brick using silica from Southern Illinois. The work was carried on successively by C. H. McClure[2], T. R. Ernest[3], and R. F. Williams[4] during the following years. Although these men studied mainly the technical side of the preparation of sand-lime brick with a view to finding an application for Southern Illinois silica, the by-reactions due to the presence of substances other than silica and lime, such as clay and feldspar, were also the objects of investigations.

This part of the work was the main object of A. W. Beemer's[5] thesis in 1910. Among the mixtures studied by Beemer is that of lime and feldspar. Beemer came to the following conclusions: "When a mixture of $Ca(OH)_2$ and feldspar is acted upon by steam, a combination is affected. The extent of the combination of the different components varies according to the proportion of the ingredients used. There is probably a complex calcium aluminium silicate formed

as is the case in the mixture $Al(OH)_3$, $Ca(OH)_2$, and SiO_2; and in instances where the percentage of $Ca(OH)_2$ is high, some calcium aluminate is undoubtedly formed.

From the foregoing it was apparent that if partial decomposition of the feldspar had taken place, some of the potassium had probably changed to a soluble salt, and this was shown to be true by a few qualitative tests. Practically no quantitative potassium determinations were made, and the subject was left at this point.

The investigations had however shown that it might be possible to bring the decomposition of feldspar by lime so as to render the potassium in feldspar soluble. To determine the extent of the decomposition of feldspar by lime under pressure, and the conditions under which the decomposition reactions occur at a maximum, remained to be done. The study has interest from a purely chemical standpoint, but more so as affording a possible means of extracting for fertilizer use the enormous quantities of potassium, now tied up in feldspathic and other potassium bearing rocks.

The work which is the subject of this thesis was accordingly started in the fall of 1910. The investigations were carried on with the assistance of Dr. McFarland of the department of applied chemistry. The main purposes of the work were the following.

1. A review of the current literature on the potash problem in the United States, on the sources of potash

and especially on the extraction of potash from feldspar, comprising also an investigation of the patents issued by the U. S. Bureau of Patents on means of extracting potash from feldspar.

2. An experimental investigation of the possibility of extracting potassium from feldspar by the action of lime under steam pressure.

3. In case of success in the experimental work, the preparation of some of the feldspar lime mixture treated by steam pressure to be tested as fertilizer by the Agricultural Experiment Station, U. of I.

FIRST PART.

Potash salts are used extensively in the United States in an almost endless series of chemical industries and manufactures. The fertilizer industry ranks first in the potash consumption, but smaller quantities, by no means negligible, are used in glass manufacture, soaps, explosive powders, and in chemical industries such as the manufacture of dyestuffs, cyanides, bleaching powder, alum, and in the preparation of other numerous salts.

Practically all the potash salts of mineral origin consumed in the United States at present are imported from abroad, chiefly from Germany. The German potash industry is controlled by a syndicate and difficulties have repeatedly arisen between the U. S. government, representing the interests

of the American potash industries, and this German syndicate.[6,7] The importance of the problem can be better understood from the value of the potash salts imported. The Bull. of the U.S. Geol. Survey for 1911 on "Potash Salts, their uses and Occurrence in the United States", by W. C. Phalen[8] gives the value of the potash salts imported, and it shows an increase from $3,700,000 in 1900 to $5,500,000 in 1905, and $8,400,000 in 1910. During the same period the value of the potash industry in the U. S. increased from $520,000 in 1900 to $1,980,000 in 1905 and probably surpassed $4,000,000 in 1910.

Although soluble potash salts occur in many forms in the United States, none of the deposits are of large practical importance. According to F. W. Clark[9] the percentage of K_2O in the earth's crust is 3.00, which is the average results of 1434 determinations. The largest amount of potash is found in feldspathic rocks and runs up to 16.8 percent K_2O in pure orthoclase feldspar. The potash of these rocks has generally been supposed to be tightly locked up. Ten or even five per cent potash rock would be highly valuable as a fertilizer were there known any cheap method of making the potassium available for immediate use of the growing plant.

The extraction of potassium from feldspar has thus become the object of many researches, but although patents have been taken on some of the processes, none of the investigations have been completely successful.

A large number of the patents taken out seem to be merely claims based upon a supposition that the decomposition of feldspar would take place under certain conditions, and in most cases no experimental work has been carried out.

The methods proposed for the decomposition of feldspar may be grouped as follows.

I Fine grinding.

II Acid treatment.

III Fusion, in which the feldspar is fused in the presence of some reagent.

IV Heating method, the crystalline feldspar being transformed by heating to an amorphous condition.

V Pressure method, the feldspar being heated under pressure in presence of some reagent.

I Fine grinding process:

The fact that water alone extracts a very small amount of potassium from feldspar has been recognized, and it was suggested that very fine grinding might permit the use of feldspar as fertilizer. The best investigations along this line were made by A.S. Cushman and Provost Hubbard, chemists in the U.S. Dept. of Ag., Office of Public Roads. The results of their work is published in a series of bulletins,[10,11,12,13,14,15,16] and show that dry ground feldspar gives only from .08 to.12 % K_2O soluble in water. Dry grinding with gypsum and CaO increased the amount of solution in water to .33 and .63 per cent. respectively.

The amount of extraction was also increased by fine grinding and wet grinding, by presence of electrolytes in solvent water and by electrolytic removal of the dissolved alkali. A.S. Cushman took in 1907 patent No. 851,922 based on the electrolytic extraction of potassium from feldspar. This patent is described as follows:[8,17]

Feldspathic or other potash bearing rock is ground to fine powder, slimed with water and placed inside of a suitable wooden container, which is then set inside of another larger vessel. Water is now placed in the other vessel and electrodes inserted so that the inner or slime chamber becomes connected with the positive pole and the outer chamber with the negative pole. A current of electricity from a dynamo is then turned on. When this is done the potash, soda, and other bases are partially set free from the combinations with alumina and silica in which they exist in the feldspathic rocks.

Under the influence of electrolysis the soluble bases pass through the wooden partition and the water in the outer vessel becomes alkaline, owing to the accumulation of potassium and sodium hydroxide. The electrical resistance of the cells arranged in this way is so high that only a small fraction of an ampere passes through under a potential of 110 volts. After a certain percentage of the alkali has been extracted in this manner the action slows down, and it has been found necessary to devise methods to accelerate it.

Dr. Cushman has discovered two methods of accelarating

the decomposition of the rock slime and hastening the extraction of the potash. (a) By a suitable grinding or churning arrangement the slime in the inner chamber can be kept in a continual agitation, which causes the necessary reactions to go on more rapidly. (b) If a small quantity of hydrofluoric acid is added to the slime a very great acceleration in the rate of decomposition and extraction is obtained, and it is possible in a reasonably short length of time to make a complete extraction of all the potash contained.

If instead of caustic potash it is desired to make various salts of potash such as are in ordinary use for fertilizers and other purposes-that is nitrate, sulphate, and phosphate-the corresponding acids (nitric, sulphuric, hydrochloric and phosphoric) are fed in a dilute form into the outer or so-called cathode chamber fast enough to neutralize the caustic alkali as it forms. By varying the amount of acid added the resistance of the cell can be controlled and the decomposition of the rock carried on under the best and most economic conditions."

The increase in extraction by electrolytic treatment and by wet grinding can be explained as follows. The aluminium silicate compounds formed on the liberation of the alkaline salt, hydrolyse and form $Al(OH)_3$ which remains as a jelly like, colloidal coating on the surface of the individual grains. This coating absorbs a large portion of the alkali and prevents its solution in water, even though the water action be long continued. The factors mentioned which increase the solubility of the potassium are those which either cause the

removal of the colloidal substance such as wet grinding and electrolysis, or cause the liberation of the alkali from the colloid such as the electrolytes. Fine grinding aids materially by exposing a vastly larger surface to the solvent action of water. These factors taken together allow the dissolved alkali to be continuously removed and more must pass into solution to reestablish equilibrium. The result is a greatly increased extraction.

II Acid treatment:

The effect of an electrolyte towards increasing the amount of potassium made available has already been pointed out. All acids then act in a similar manner and an increased extraction is obtained on the addition of all acids. The increase is small and the potash extracted increases with the concentration only to a certain limit. It is interesting, however, to review the different methods proposed in which feldspar is treated with acid.

In 1882, John Spiller[18] proposed the manufacture of potash alum by heating a mixture of fluospar, feldspar and sulphuric acid. Alum and SiF_4 would be obtained. The SiF_4 could be passed in water to give SiO_2 for polishing powder and fluosilicic acid.

W, T, Gibbs[19] took out in 1904 a German patent for decomposing silicates such as feldspars and micas by means of mineral acids as sulphuric with the addition of fluosilicic acid in small quantity. By a separate process the fluosilicic

acid is recovered from the fluid. It is supposed to play the part of a catalytic agent and an addition of 2 - 4% fluosilicic acid to other mineral acids is sufficient.

The use of hydrofluoric acid for the decomposition of feldspar by A.S. Cushman has already been recalled. Cushman used hydrofluoric acid not only in electrolytic extraction of potassium but tried a few experiments in which the acid was made to react directly with the feldspar. Only a few data were obtained, and Cushman urged further investigation in this field.

In connection with the decomposition of feldspar by acids, it might be interesting to point out the possible use of feldspar over which SO_2 fumes from smelters have been passed. A similar decomposition of clays and the utilization of the smelter smoke in preparing sulphates has been proposed.[20]

III Fusion methods:

In this method the feldspar is fused in the presence of some reagent which is in most cases salt or lime. Four English patents[21] to Tilghman (1847), Newton (1856), Ward (1857), and Rhodin (1901), and one U. S. patent in 1908 to Ralph Mackee[22] have been issued along these lines. Rhodin claimed that an extensive business based on his process had been started, and that 80-90% of the K_2O was rendered soluble. Nothing further was ever heard from this and it is probable that if any attempt has been made to put the process on a commercial basis, it has failed.

Fusion experiments were also tried by Cushman and Hubbard[10] with a large number of reagents. $CaCl_2$, $NaNO_3$, Na_2CO_3 mixed with $NaNO_3$ and KNO_3 all react with feldspar when fused with it and render some potash soluble. None are economical, however, and give any promise commercially.

IV Heating Method:

The feldspar is heated to a high temperature and cooled rapidly. By this process the insoluble crystalline potassium compounds break down leaving available potassium salts.

Patent No. 959,841 has been taken out on this process by Franklin R. Carpenter[23] of Denver, Colorado. He describes his method as follows: "The ease of solubility, I accomplish by first heating crushed granite or other rocks in which potash minerals occur to a high heat, even to the fritting or fusing of the same, either with or without flux, and then suddenly cooling the same in water, which brings about such a change in their composition or molecular construction that the formerly insoluble potash minerals become readily soluble in certain acids, notably hydrochloric, hence directly available for plant life. After this heating, fritting, or fusing and subsequent chilling, the material is ground to a fine powder and used as a fertilizer for soils in the manner of any other fertilizer."

Carpenter claims that by this treatment, he not only brings disagregation, but that he changes the insoluble crystalline potash compounds which exist in the rocks to amorphous forms which are soluble and available for plant life. The heating has also the effect of facilitating the pulverizing

of the rocks which is an important factor in the extraction of potash.

A patent involving a somewhat similar process was taken out by Swayze[24]. After subjecting feldspar to the heating process, he treats it further with a compound of potassium under pressure. This leads us to a new process.

V Pressure method:

In this method the feldspar is heated in the presence of some reagent under high steam pressure. Schäcke[25] in 1905 and Pohl[26] in 1906 took patents on this method of making fertilizers from feldspar. The process involved is best described in a patent already mentioned taken 1907 by Aurelius J. Swayze[24] of Great Meadows, N.J. on "Extraction of Potassium Compounds from Feldspar." The amorphous feldspar obtained by the heating process is transferred to a closed vessel and mixed with a solution of a potassium compound, preferably caustic potash. The mixture is then heated so as to maintain a high pressure in the vessel. After a certain length of time the solution is withdrawn and the potassium extracted with water. Swayze claims that by heating the mixture under pressure, a solution of potassium silicate and aluminate is formed.

The process as described would permit the extraction of the potash from the feldspar together with the potassium from the caustic potash added. The rather large quantity of KOH which is necessary to form a solution of 1.2-1.3 specific gravity required to decompose the feldspar does not permit an

economical use of the mass as fertilizer. It is necessary to extract the potassium and handle a large bulk of material nine tenths of which is a waste product, and it is rather doubtfull whether the process could be successfull from a commercial standpoint, even if practically complete decomposition of the feldspar was obtained.

A patent in which a gaseous reagent was used under pressure was taken in 1904 by Henry S. Blackmore of Mt. Vernon, N.Y. for a process of extracting alkalies from insoluble silicious combinations. The reagent used is H_2CO_3, but the use of SO_2 is suggested, both reagents being subjected to varying pressures. When CO_2 is used the decomposition is facilitated by the addition of $CaCO_3$ and the process taking place would be illustrated by the equation:

$$K_2SiO_3 + CaCO_3 + H_2CO_3 = CaSiO_3 + 2\ KHCO_3$$

Having thus reviewed the methods and reagents used to bring about the decomposition of feldspar, it will now be possible to carry the experimental work under the best conditions. Should experimentation confirm the fact that the potash extraction is increased under conditions pointed out by the literature the purpose of this thesis will be to combine as far as possible the action of these conditions to that of the lime so as to obtain the maximum extraction.

PART II

Experimental work was accordingly started in the fall of 1910. It was necessary to devise first some method of measuring the potassium extracted. The chloroplatinate method, besides of having the inconvenience of taking much time was found to be prohibitive because of the high cost of the chloroplatinic acid. This can be better understood if one considers that a couple hundred determinations of potassium would have to be made, and in many cases in the presence of large quantities of sodium.

A volumetric method being usually much more rapid than a gravimetric method, it was thought that a volumetric determination of the potassium would be more satisfactory. The cobalti-nitrite method was accordingly investigated. Little being known of this method and the literature on the subject being filled with controversies, it was necessary to compare at first the results obtained by this method with those obtained by the chloroplatinate determination.

The cobalti-nitrite method as used is that proposed by Adie and Wood[28] and modified by Bowser[29,30] Drushel[31] and Shedd[32,33]. As adopted the method is as follows: The solution containing the potassium salt is treated with a rather large excess of sodium cobalti-nitrite, $Na_3Co(NO_2)_6$ solution acidified with

acetic acid.

The potassium sodium cobalti-nitrite $K_2NaCo(NO_2)_6H_2O$ which precipitates is filtered off on a Gooch crucible. The potassium cobalti-nitrite is then oxidized with excess of standard $KMnO_4$. Standard oxalic acid is added in excess and the excess titrated back to color with $KMnO_4$. From the total amount of permanganate used, that equivalent to the oxalic acid used is subtracted and the remainder multiplied by the factor calculated for the strength of permanganate used.

If NH_4 salts are present in the solution containing the potassium, it is necessary to evaporate the solution to dryness and ignite until all ammonium salts are expelled, for ammonium salts give an insoluble ammonium sodium cobalti-nitrite corresponding to the potassium salt. Other elements present in lime and feldspar such as Na, Ca, Mg, Al and Fe do not interfere with the precipitation of the potassium.

A comparison of the results ofthe cobalti-nitrite method with those of the chloroplatinic method is given below.

	I		II		III	
	a.	b.	a.	b.	a.	b.
			Grams.			
K_2O Cobalti-nitrite method...	.0105	.0107	.00357	.00351	.00261	.00268
K_2O Chloroplatinate method...	.0104	.0104	.00354	.00356	.00263	.00264

These results show that the cobalti-nitrite method can be used with an accuracy of at least two or three percent when the chloroplatinate results are taken as standard. Since variations in the process of treatment and of manipulations are

capable of giving larger errors than the ones given above, the method fulfills satisfactorily the required accuracy. This method was used in all the following determinations of the soluble potassium.

The feldspar used in this work was Brandywine Summit feldspar of the following composition:

	Per Cent.
SiO_2	70.02
Al_2O_3	17.89
Fe_2O_3	0.21
CaO	0.98
MgO	0.16
K_2O	8.71
Na_2O	1.61
Loss on ignition	0.38

Practically all the feldspar as used passed a 100 mesh sieve and 30% passed 150 meshes. The lime used was common lime burned at 1200^{0} C for 2 hours and slaked with hot water. The dry powdered CaO was made to pass a 100 mesh sieve, and was found to contain 0.21% K_2O.

In all the mixtures used, enough water was used to slake the lime, and just enough excess of water added to permit the molding of the mass into briquettes. Portions of these briquettes, which had been in most cases subjected to further treatments, were taken for the determination of available potassium. This determination was made according to the method

adopted by the International Congress of Applied Chemistry Of Berlin[34] in 1903, which consists of adding 10 grams of the substance in which the available potassium is to be determined to 300 cc. of distilled water and boil half an hour. After boiling the residue is filtered off, the solution made to 500 cc, and portions taken for the determination of potassium. This method was used in every case without variation if not otherwise stated.

Having determined the methods to use in the following work, the investigations were to be carried on as follows:

1. Determination of water soluble potassium in raw feldspar.

2. Determination of the quantity of lime which gives highest amounts of soluble potassium.

3. Determination of available potassium in thebest mixture before further treatment, and investigation of the effect of steam pressure and of variations of pressures on that mixture.

4. Effect of electrolytes and acid extraction.

5. Effect of heating feldspar previous to any treatment, with or without quenching.

6. Effect of wet grinding to very fine state.

7. Effect of steam pressure on slurry mixture instead of briquettes.

1. Determination of Water Soluble Potassium in Raw Feldspar.

Before investigating the effect of any treatment on feldspar, it was necessary to determine the amount of potassium in feldspar which is water soluble, for although the feldspar is almost insoluble, small quantities of potassium and sodium go into solution. The quantities do not vary according to the amounts of potassium and sodium salts present, low potash feldspars having often more available potassium. Ten grams samples were taken for these determinations, and the available potassium extracted by the method stated, boiling the sample with 300 cc. distilled water for 1/2 hour. The following results were obtained:

	a.	b.
Per Cent K_2O extracted from sample.....	.0066	.0070
Per cent of total K_2O in sample........	.0740	.078

These results are in accordance with Cushman's values[13]. Cushman states that the amount of available K_2O in feldspar seldom reaches over .12 % of the total potash in the sample.

2. Determination of the Quantity of Lime Which Highest Amount of Soluble Potassium.

To investigate the effect of different quantities of lime on the decomposition of the feldspar, mixtures of varying compositions were prepared. The mixtures were moulded into briquettes with as little water as possible, the briquettes dried in an oven at 100° C and subjected to steam pressure

at 120 - 130 lbs., for 15 hours. After treatment the briquettes were powdered to pass 100 meshes sieve, and ten grams samples taken for the potassium extraction. The available potassium was determined by the usual method.

Sample No.	CaO %	Feldspar %	K_2O extracted in % of the Sample. I	II	III	K_2O extracted in % of total K_2O. Average.
2	20	80	.434	.427	.462	6.1
3	33 1/3	66 2/3	.886	.864	.876	14.6
4	50	50	.676	.694	.690	15.3

From these results it can be seen that the greatest extraction in% of the total potash present was given by the 50 % mixture, but that the increase in potassium made available over that liberated by the 33 1/3 % CaO is small. Moreover, for the same bulk of material, the amount of K_2O available is about 22% greater in case of the 33 1/3 % CaO mixture than in the 50 % mixture. For this reason and because of the low cost of feldspar it would be evidently more satisfactory to use the 33 1/3 % CaO mixture, were the materials to be used as potash fertilizers. Our purpose being, however, primarily to extract the greatest amount of potassium from the feldspar, the 50 % mixture was selected for further investigation.

3. Effect of Steam Pressure.

The effect of steam pressure was next investigated. The available potash of this 50 % mixture before any treatment was determined, and is recorded under No. 5. It was then possible to determine the effect of heating under pressure and drying. In sample No. 6 the mixture was dried at 100^0 but not treated further, the effect of drying being thus obtained. The effect of heating under steam pressure and of variations of pressure was further brought out by samples No. 7, 8, and 9. The following results were obtained:

Number Sample	Treatment	Steam pressure in atm.	Time in hours.	K_2O available: In % of sample.		In % of total sample.
				I	II	Average.
5	Raw			.0158	.0162	.35
6	Dried at 100^0			.186	.197	4.2
7	Dried and steamed under pressure	25-30	1	.656	.642	14.4
8	"	20-30	9	.997	.984	22.0
9	"	25-32	5	1.65	1.55	35.00

The preceeding data have established the following facts:

a. Very little action takes place between feldspar and lime when the mixture is not further treated. The potassium being extracted by boiling, it is probable that no action takes place at first in the mixture, but that a little action goes on during the boiling period.

b. An appreciable action takes place during the drying period.

c. The action of the lime increases greatly under the steam pressure and to a certain extent increases with the pressure used and with the length of heating. The increase of the action of the lime with the length of heating holds only to a certain limit, after which longer treatment has little influence. The reaction increases probably with higher pressures, but no means were at hand to verify this statement above 35 atmospheres.

4. Effect of Electrolytes:

The next step in the investigation of means to bring the decomposition of the feldspar by lime was to determine the effect of the addition of electrolytes such as $CaCl_2$ and NH_4Cl to the lime feldspar mixture. These electrolytes were added before treatment under steam pressure as suggested by analogy with the Lawrence Smith method[36] used to decompose silicates, or after treatment as pointed out by Cushman[14].

A first set of experiments was carried on adding the electrolytes before treatment under steam pressure. The mixtures prepared, together with the results obtained are given below. The mixtures were heated 15 hours at 120-130 lbs. steam pressure.

Number Sample	Cao	Feldspar	NH_4Cl	$CaCl_2$	K_2O available In % of sample. I	II	In % of Total. Ave.
	Parts						
10	20	70	10		.165	.163	2.6
11	20	70		10	.510	.495	8.1
12	45	45		10	.587	.608	14.8
13	45	45	10		.482	.467	11.5

These results show the following facts.

a. $CaCl_2$ acts as inert matter. This can readily be seen by a comparison of the potash extracted from samples No. 12 and No. 4.

b. NH_4Cl decreases the amount of available K_2O. This result seems to be surprising at first. It should however, be remembered that thereaction taking place here is probably different from the one on which the J. Lawrence Smith method is based and which is represented as follows:

$$2KAlSi_3O_8 + 6CaCO_3 + 2NH_4Cl = 6\ CaSiO_3 + 6CO_2 + Al_2O_3 + KCl + 2NH_3 + H_2O.$$

In the Lawrence Smith method the mixture is dry and is heated to a high temperatureto the sintering of the mass. In the method used in this work the mass is heated only to a comparatively low temperature, and it is probable that the only reaction taking place with the NH_4Cl is the liberation of the NH_3 and the formation of $CaCl_2$. This $CaCl_2$ as was shown by No. 11 and 12 acts as inert matter. At thesame time the amount of Cao present is decreased by the quantity used up by the NH_4Cl, and hence having less CaO to act on the feldspar, less

potassium will become water soluble.

These data have also pointed out the fact that $CaCl_2$ has no effect when added to the solution after treatment, since the $CaCl_2$ is not decomposed during the treatment under steam pressure and it has already been seen that there is no increase in the available potassium extraction. It was necessary to investigate whether the NH_4Cl would have any effect when added to the solution before boiling and after the treatment under steam pressure. Sample 9 was used for this purpose and boiled with 10 % NH4Cl 1/2 hour and gave an average of 1.02 % K_2O in the sample, or 25.2 % of the total K_2O in the mixture. Water extraction without NH_4Cl giving 35.+ % $K_2O$of the total K_2O in the sample, it is seen that in this case also the NH_4Cl has the effect of decreasing the amount of available potassium extracted from the feldspar. These facts are not in accordance with Cushman's[14] theory that the presence of electrolytes increases the amount of potassium made available on treatment of feldspar. It is however possible that since the lime has an effect of its own, which is probably destroyed by the presence of the electolytes, these electrolytes have some effect on the feldspar, which could not be estimated in the preceeding experiments. It seems however established that in the presence of lime, the electrolytes used do not increase the available potassium extracted from feldspar.

ACid Extraction:

In connection with the effect of electrolytes,

the effect of acids was to be investigated. The effect of the acid will depend upon its concentration. Dilute HCl gives, for example, at first $CaCl_2$ and its action will be appreciable only at stronger concentrations. Experiments were carried on extracting the potassium from some of the preceeding samples with a solution containing 10 cc. concentrated HNO_3 in 300 cc. H_2O or approximately N/5 solution. The following results were obtained:

Sample	Average K_2O extracted:	
Used No.	In % of sample.	In % of total K_2O.
1	.90	20.0
2	.89	12.4
3	.70	11.7
10	.17	2.7
11	.52	8.2
12	.42	10.4

In the three first samples in the mixture of lime and feldspar alone there is a marked increase of extraction due to the effect of the acid. In the three last samples in which NH_4Cl and $CaCl_2$ had been added, there is no effect of the acid in the two cases, and in the last sample a decrease of the potassium extracted.

A set of experiments were carried on later using a 50 % mixture of which the feldspar had been previously heated to 1150°C, and the mixture treated under 8-10 atmospheres of steam pressure. Ten per cent HNO_3 was used and the results are

recorded under sample No. 14. The residue from the acid extraction was boiled with 300 cc. H_2O, the results being recorded under sample No. 15.

Sample Number.	K_2O available: In % of Sample. I	II	III	In % of Total K_2O. Average.
14	1.68	1.63	1.51	36.0
15	.16	.16	.17	3.6
				39.6

The effect of HNO_3 is then to increase the extraction 6 %.

5. Effect of Preheating and Quenching:

The effect of heating feldspar previous to its treatment with lime was next investigated at a series of temperatures. Part of the feldspar was quenched at each temperature by suddenly immersing the feldspar in cold water and rapidly filtering off the residue. The potassium was determined later in the residue and in the portions of the water taken for quenching.

Samples 16-22 give the data for the unquenched feldspar, 23-28 for quenched feldspar, and water of quenching. The unquenched samples and the residue from the quenched samples were made into 50 % mixture briquettes in the usual way and steamed under pressure at 8-9 atmospheres for 18 hours.

Sample Number	Temperature Reached. Degrees C.	K_2O Available: In % of Sample.			In % of Total K_2O.
		I	II	III	Average.
16	550	.767	.793	.741	17.1
17	650	1.080	1.090	1.150	24.4
18	750	.893	.934	.925	20.5
19	850	.676	.696	.754	15.5
20	950	.814	.831	.848	18.5
21	1050	.865	.857	.857	19.1
22	1200	1.320	1.337	1.357	29.8

Sample Number.	Temperature Reached. Degrees C.	K_2O available: In % of Sample.		In % of Sample In H_2O of Quenching.	Total K_2O available in % of total K_2O.
		I	II	Average.	Average.
23	550	.932	.965	.185	25.2
24	650	.874	.874	.134	20.2
25	750	1.136	1.122	.106	25.1
26	850	1.165	1.136	.127	25.6
27	950	1.064	1.109	.089	25.0
28	1050	.815	.836	.043	20.3
29	1200	1.089	1.078	.047	25.1

From these data it can be seen that in theunquenched series, two maxima and one minimum amount of K_2O extracted were obtained. The first maximum is somewhere near 650^0 C. A second maximum extraction was obtained at about 1200^0 C. This was the highest temperature that could be reached in the muffle

furnace used. It is possible, however, that higher temperature would have given increased extraction. A minimum occurred near 850° C. The presence of these maxima and minima seem peculiar at first sight. They are, however, in accordance with the properties of the feldspar, such as the shrinkage at different temperatures. In the measurement of "thermal properties of the feldspars" by Day and Allen[35] maxima and minima have also been constated. It seems that the crystalline compounds found in the feldspar at ordinary temperatures break down when heated, to form at first other crystalline salts and finally are changed to amorphous compounds. It is interesting to note that when the feldspar was suddenly quenched after heating an extraction almost identical is obtained at all temperatures except in the neighborhood of the temperature at which maxima were observed in case of non-quenched samples. From this it would seem that the action taking place in the feldspar at different temperatures is similar to that of some hydrates breaking down to reform compounds containing a smaller number of molecules of water and finally leaving the dehydrated compound.

6. Effect of Wet Grinding:

The effect of grinding the feldspar to a very fine state in view of increasing the amount of potash liberated was to be the object of the next test. The effect on a 50% raw mixture was first investigated. Ten grams were placed in a ball mill with 100 CC. of water and ground for three hours. After this time the contents of the ball mill were washed into

a flask and enough water was added to bring the content of the flask to 300 cc., and the mixture was boiled as usual for one half hour. The results are given under Sample No. 30. A similar process was next carried on with a treated 50 % mixture from Sample No. 8, in which the mixture had been heated 9 hours to 20-30 kilograms pressure. The results obtained from this mixture are recorded under Sample No. 31.

Sample Number.	K_2O Available: In % of Sample. I	II	In % Soluble K_2O. Average.
30	.12	.11	2.6
31	.42	.45	9.7

By comparing 5 and 30 it can be seen that wet grinding increased the amount of potash extracted from the 50 % mixture to an appreciable extent. Sample 31 gives, however, not only no increase, but in the contrary a decrease of about 50 %.

7. While investigating the effect of steam pressure in the decomposition of the feldspar, it was thought that perhaps the effect might depend on the surface ofthe mixture exposed. To ascertain this fact 50% mixtures were prepared which were not moulded into briquettes, but to which an excess of water had been added so as to form a slurry . A thin layer of the mixture was subjected to the action of steam under pressure.

After treatment the potash was extracted as usual. The potash was extracted again from the residue by a second boiling with water.

Sample Number.	Treatment.	K_2O Extracted: In % of Sample, by First Extraction.			In % of Sample by second Extraction.		Total of both Extractions in % of Total Potash.
		I	II	III	I	II	Average. %
32	3 hrs. 20-30 atmos.	.92	.91	---	.08	.08	22.2
33	2 hrs. 30 atmos.	1.08	1.15	.109	.12	.11	26.9
34	4 hrs. 25-30 atmos.	.89	.90	.90	---	___	20.0

By comparison of these results with those from 7, 8, 9 it can be seen that the use of a slurry mixture does not appreciably increase the amount of potash extracted. The results from the slurry mixtures and briquettes depend largely on the pressure reached and at the same pressure and for equal time of heating, the data obtained would probably be very nearly the same.It would however be very difficult to regulate the conditions so as to permit an accurate comparison. It was also constated that an appreciable leaching of the slurry had taken place in thebomb, in which the mixtures were heated under steam pressure. Qualitative determinations of the potassium in the condensed water from the bomb, show that the leaching was however small. Quantitative determinations were made later to determine the amount of leaching from

50 % mixture briquettes and gave an average of .109 % K_2O, which would give an increase of 2.4 % in the extraction of the total K_2O in the sample. As can be seen this leaching did not appreciably change the results.

SUMMARY AND CONCLUSIONS.

1. When feldspar is heated in the presence of lime under high steam pressure, a decomposition of the feldspar takes place, and some of the potash in the feldspar becomes water soluble.

2. Under uniform conditions, the decomposition of the feldspar seems to be greatest when the amount of lime is equal to that of the feldspar.

3. The action of the lime on feldspar increases to a certain extent with the steam pressure and the length of treating. Very little action takes place at ordinary temperature, but an appreciable reaction takes place even on simply drying the mixture at 100^0.

4. The addition of electrolytes such as NH_4Cl, $CaCl_2$ to the 50 % mixture does not increase the amount of caustic potash rendered water soluble. Acid extraction with HNO_3 gives higher results for potash when $CaCl_2$ and NH_4Cl were not originally present.

5. The amount of potassium rendered water soluble by the action of lime on feldspar can be increased by heating

the feldspar before treatment. The best temperatures at which the feldspar should be heated are 650^0 or 1200^0 C. when the feldspar is left to cool slowly. If the feldspar is to be quenched, it is best to heat it to 580^0C. without exceeding this value.

6. Wet grinding ofthe feldspar before treatment seems to be also beneficial, although to only a small extent. Wet grinding of the 50 % mixture after treatment under steam pressure seems to have the opposite effect, although this fact is not well understood.

7. The use of a thin slurry mixture instead of briquettes does not appreciably increase the amount of potash made available.

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